

*Problems Bearing on Residual Affinity.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

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[PLATE 2.]

Valency implies the existence of something equivalent to the possession by an atom of points of attachment, and is inseparable from the idea of chemical combination ; but it must not be confused, as has often been done, with the force acting at those points. The properties of a mass of matter are the sum of those of its constituents, and, since molecules combine together, the affinities and valencies effecting their union must be those of the constituent atoms. The satisfaction of such additional valencies will represent a comparatively small expenditure of energy, for, even when principal valencies are concerned, as when an element forms pairs of oxides or halides, the heat evolution on combining with the additional oxygen atom is, on the average, only 38 per cent. of what it is on combining with the first atom or atoms (17 cases), and 52 per cent. in the case of the halides (10 cases).<sup>\*</sup> At this rate residual affinity must soon become reduced to a quantity insufficient for the attachment of another free atom, but might still be sufficient to unite with it if it were already in combination, and had only its own residual affinity available. Platinum is hexavalent in  $\text{Cl}_4\text{Pt} < \begin{smallmatrix} \text{ClK} \\ \text{ClK} \end{smallmatrix}$ , though  $\text{Cl}_6\text{Pt}$  cannot exist. It is, therefore, only in so-called molecular compounds that the highest valencies of an atom can be expected, though no fundamental differences can be imagined between the higher and the principal valencies ; this is admitted even by those who have coined a distinctive name for the higher valencies (*e.g.*, Werner's "co-ordination values").

The general rule that additional valencies come into existence in pairs is not invalidated by certain apparent exceptions. Thus, the most stable arrangement of five atoms round a central one is two in one plane, and three in the plane at right angles ; according as the positions occupied are those in the one, the other, or both planes, the atom will show valencies of 2, 3 or 5, and by the suppression or development of pairs of valencies, other values of 1, 4, 7, 9, etc., might be shown.<sup>†</sup>

<sup>\*</sup> The halides of gold are exceptions, the heat of formation per halogen atom increasing with the proportion of halogen. This indicates that there is no change of valency, the aurous halides being  $\text{X}-\text{Au}=\text{Au}-\text{X}$ . The case is comparable with that of  $\text{C}_2$  combining with  $\text{H}_2$ ,  $\text{H}_4$  and  $\text{H}_6$ , where the evolution per atom of hydrogen is -23,885, -1645 and +4567, respectively.

<sup>†</sup> 'Journ. Chem. Soc.,' 1893, p. 1069.

Alone of the better known elements, carbon and hydrogen appear to exhibit no higher valencies,\* and can consequently be built together to an extent unknown in other cases. This does not negative the view that carbon may sometimes exhibit a certain amount of residual affinity, sufficient to explain such facts as those observed by Thiele,† without attributing to the doubly linked atoms any additional "partial" valencies. Though Thomsen's conclusions as to the values of double and treble linkage cannot now be accepted, these doubtless represent less energy than two or three single links.‡ The existence of such multiple linkage has been contested on the ground of the inferior stability of the compounds containing them; but decomposition of a substance containing, for instance,  $\equiv \text{C}-\text{C} \equiv$  means that an advantage is gained by substituting the linkage  $\text{X}-\text{C}$  for  $\text{C}-\text{C}$ ; hence, the more carbon-carbon linkages there are for such substitution, the less stable will be the compound.

Thomsen's determination of the thermal value of substituting  $\text{CH}_3$  for  $\text{H}$ , when seven out of the 48 cases are omitted, is 7814 cal., the variation indicating a probable error of  $\pm 1537$  for any one value, of which, judging by the difference between duplicates, 1082 cal. is accounted for by errors of measurement, leaving only 455 for errors due to imperfect purity. Hence this value is a constant within the limits of experimental error; but it may well be questioned whether it is absolutely constant, for it varies between the wide limits of 4320 and 10,870 cal.§ (or 730 and 13,810 cal., if the seven exceptional cases are included); added to which, absolute constancy would imply that the carbon atom is, as it were, divided into four watertight compartments, the happenings in one of them being unaffected by those in the others; which is quite opposed to known facts.

With the monochloro-derivatives the constant, 2464 cal., varies between 800 and 5190, the probable error being  $\pm 1439$ , of which 1080 is attributable to measurement errors.

With radicles possessing residual affinity, such as  $\text{Cl}$  or  $\text{OH}$ , the introduction of the second unit results in an increased heat evolution, since their residual affinity can then come into play, whilst the introduction of the fourth unit results in a notable decrease, the four units then forming a ring in equilibrium round the nucleus, and being unable to draw closer to each other. The

\* The recently established combination of paraffins with soaps (*loc. cit.*, vol. 111, p. 86) may be an instance to the contrary.

† 'Annalen,' vol. 306, p. 87; vol. 308, p. 213.

‡ Armstrong, 'Phil. Mag.,' vol. 23, p. 73 (1887); Pickering, *ibid.*, p. 109.

§ The variation appears insignificant when the values are expressed as differences in the heat of combustion of homologues, for such differences each contain 165,900 cal., representing the heat of combustion of  $\text{C}$  and  $\text{H}_2$ .

effect when the third unit is introduced cannot be predicted, and seems to vary with circumstances.

Table I.—Heat Evolved on the Successive Substitution of the same Radicle.

| Substitution.                          | First.  | Second. | Third.  | Fourth. | Maximum difference. | Probable error.* |
|----------------------------------------|---------|---------|---------|---------|---------------------|------------------|
| CH <sub>3</sub> for H                  |         |         |         |         |                     |                  |
| In CH <sub>4</sub> .....               | 6,230   | 5,970   | 6,760   | 4,820   | 1,940               | ± 2,361          |
| In C <sub>2</sub> H <sub>4</sub> ..... | 5,350   | 6,860   | 7,730   | —       | 2,380               | ± 1,034          |
| Cl for H†                              |         |         |         |         |                     |                  |
| In CH <sub>4</sub> .....               | 800     | 1560    | —       | 3,080   | 3,880               | ± 858            |
| In C <sub>2</sub> H <sub>6</sub> ..... | 2,150   | 3,546   | — 275   | —       | 3,821               | ± 1,720          |
| In C <sub>x</sub> H <sub>y</sub> ..... | 2,464   | 3,656   | — 2,230 | — 3,471 | 7,127               |                  |
| OCH <sub>3</sub> for H                 |         |         |         |         |                     |                  |
| In CH <sub>4</sub> .....               | 27,020  | 37,730  | 41,350  | —       | 14,330              | ± 1,302          |
| CH <sub>3</sub> for H                  |         |         |         |         |                     |                  |
| In NH <sub>3</sub> .....               | — 2,927 | 2,600   | 2,570   | —       | 5,527               | ± 1,191          |
| C <sub>2</sub> H <sub>5</sub> for H    |         |         |         |         |                     |                  |
| In NH <sub>3</sub> .....               | 4,463   | 10,650  | 11,400  | —       | 6,937               | ± 1,851          |

\* Of the determinations giving the maximum difference.

† Determined directly from the heat of combustion of the compounds. Thomsen ('Untersuchungen,' IV, p. 279) adopted an indirect method, making use of certain constants which are the same in all cases, and hence reduce the apparent error. As a result, also, he got values for successive substitutions which he admits are meaningless (p. 284).

Berthelot and Ogier determined the value for CH<sub>3</sub>Cl<sub>2</sub>, but it is impossible in such a case to piece together the results of different observers using different methods.

The values for C<sub>x</sub>H<sub>y</sub> include all Thomsen's results with various hydrocarbons.

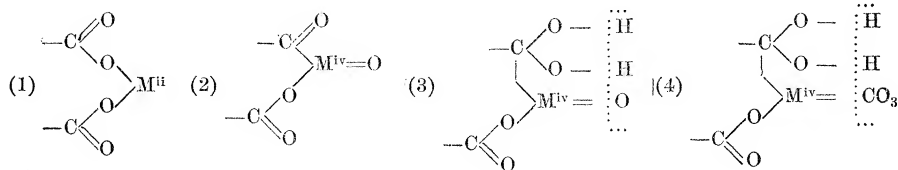
Where the element exhibiting residual affinity is in the nucleus, and the radicle introduced exhibits no residual affinity, the valency of this element may change on the first, but not on subsequent substitutions. This is so with the amines. The change of valency, which is also the explanation given by Thomsen, might be put to the test by ascertaining whether the heat of neutralisation of ammonia is 5000 or 6000 cal. less than that of the amines in the gaseous condition; for the hydrochlorides must all be similarly constituted.

Amongst the elements known to exhibit residual affinity, oxygen, nitrogen and sulphur are conspicuous. Sulphur, and the first two in the form of water and ammonia, figure in thousands of so-called molecular compounds, and their power of combining is also shown by their polymerisation, as evidenced by the exceptional heat-absorption occurring when their temperature is raised, or their state changed.\*

*Metallo-Compounds.*—Valency values higher than those usually exhibited seem necessary to explain the existence of organic salts of metals when in the metallo-condition, that is, when the metal forms part of a complex anion, and is, therefore, directly united to carbon, and unrecognisable by

\* *Loc. cit.*, vol. 95, p. 127.

the ordinary tests, as with iron in the ferrocyanides. In 40 cases, with five different acids and 13 different metals (mostly such as are usually divalent), these isomers of the normal salts have been obtained: \* (1) by precipitation of freshly prepared solutions by alcohol, (2) by double decomposition with the organic salt of an alkali metal. They appear as emulsions, drying to amorphous powders, much more soluble than the corresponding normal crystalline salts, into which they partially and gradually change in solution. This change is accompanied by a reduction in colour-intensity, where the compounds are coloured. In many cases solutions of them may be evaporated without, or with only a partial, change into the normal salt: they then yield glassy or scaly solids. The relation between the normal and the metallo-salt in its anhydrous and hydrated condition is shown by (1), (2) and (3):



*Metallo-Compounds of Alkali Metals.*—Solutions of tartrate or citrate of sodium (but not of potassium) may, on repeated trials, be concentrated at 100° beyond the point (12.6 H<sub>2</sub>O for the citrate) at which crystallisation normally occurs; they then leave glassy residues, consisting approximately of Na<sub>2</sub>T, 2H<sub>2</sub>O and Na<sub>3</sub>Cit, 4H<sub>2</sub>O, which, over sulphuric acid, dry to scaly deposits, similar to those obtained from other metallo-compounds (fig. 1, Plate 2—fig. 2 showing the normal salt—for which we are indebted to Dr. H. B. Hutchinson). The glassy residues, exposed to air saturated with moisture, absorb water 2½ times more rapidly than do the crystallised salts of the same degree of hydration. On prolonged heating of the glassy citrate at 100°, specks of the anhydrous normal citrate make their appearance, just as in the case of some cupric compounds,† and eventually spread throughout the whole; the crystallised salt, on the other hand, cannot be dehydrated at 100°.

*Ato-Compounds.*—This term has been applied to substances to which the elements composing a salt have become attached—carbonato, sulphato, etc. If the substance in question is a metallo-compound, the complex would be a metallato-compound. The salt elements [formula (4), above] would occupy

\* 'Journ. Chem. Soc.' vol. 95, p. 1409; vol. 98, p. 1837; vol. 99, pp. 169, 800, 1347; vol. 101, pp. 174, 1614, 1625; vol. 103, p. 1358; vol. 105, p. 464; vol. 107, pp. 942, 955; vol. 109, p. 235.

† *Loc. cit.*, vol. 107, p. 955.

the place of the water in the hydrated metallo-compound, which latter is really an ato-compound (hydrato). Such compounds containing  $K_2CO_3$  have been described under the name of  $\alpha$ -cupricarbonates.\* If the metal is an alkali metal they should be, and are, strongly alkaline, since they contain OM derived from a non-acidic hydroxyl (see pp. 540, 543); if the elements of an acid, instead of those of a salt, unite with the metallo-compound, the complex would be neutral.

*Combination of Acids with Organic Salts.*—When hydrochloric (or other) acid is added to potassium (or any other) carbonate in the presence of potassium citrate, no evolution of carbon dioxide occurs under conditions such as, in the absence of the citrate, would ensure a violent evolution of the gas. Series of seven experiments each, at  $15^\circ$  and  $0^\circ$ , in which the acid and carbonate were mixed in the presence of varying proportions of citrate, etc., in a closed flask connected with a manometer, showed that at an excess pressure of 200 mm. the following molecular proportions of carbonic acid were retained:  $0.4 H_2CO_3$  by  $Na_3Cit$ ;  $0.24 H_2CO_3$  by  $K_3Cit$ ;  $0.08 H_2CO_3$  by  $NaAc$ ; and practically none by potassium malate, tartrate and lactate. As the solubility of carbon dioxide in water was found to be reduced by potassium citrate, it must be  $H_2CO_3$ , and not  $CO_2$ , which combines with the salt. The complexes are, naturally, unstable, and gradually decompose.

Other acids behave in the same way. The proportions required to produce a fairly well marked acid reaction in the presence of various salts at decinormal strength, using methyl orange as indicator, and subtracting from the observed values the amount required to produce the same tint in an equal volume of water, are given in Table II. With inorganic salts, the absorption

Table II.—Equivalent of Acid producing Acidity with One Equivalent of Alkali Metal present, less that required with Water only.

| Acid.           | Water. | $KNO_3$ . | KCl.  | $K_2SO_4$ . | Pot.<br>oxal. | Pot.<br>tart. | Pot.<br>lact. | Pot.<br>cit. | Sod.<br>cit. | Pot.<br>acet. | Mean. |
|-----------------|--------|-----------|-------|-------------|---------------|---------------|---------------|--------------|--------------|---------------|-------|
| $HNO_3$ .....   | ·0004  | ·0006     | ·0008 | ·0011       | 0·46          | 0·80          | 0·64          | 0·57         | 0·31         | 0·25          | 0·17  |
| HCl .....       | ·0004  | ·0000     | ·0000 | ·0010       | 0·50          | 0·83          | 0·65          | 0·58         | 0·41         | 0·26          | 0·26  |
| $H_2SO_4$ ..... | ·0004  | ·0000     | ·0000 | ·0004       | 0·48          | 0·85          | 0·63          | 0·59         | 0·28         | 0·32          | 0·17  |
| Oxalic .....    | ·0005  | ·0000     | ·0000 | ·0008       | 0·54          | 0·97          | 0·80          | 0·66         | 0·33         | 0·33          | 0·22  |
| Tartaric ...    | ·0007  | ·0000     | ·0008 | ·0011       | 0·55          | 0·99          | 0·80          | 0·68         | 0·37         | 0·24          | 0·19  |
| Lactic .....    | ·0009  | ·0000     | ·0012 | ·0012       | 0·63          | 1·18          | 0·78          | 0·90         | 0·33         | 0·38          | 0·19  |
| Citric .....    | ·0006  | ·0007     | ·0000 | ·0007       | 0·80          | 1·43          | 1·19          | 1·05         | 0·47         | 0·38          | 0·25  |
| Acetic .....    | ·0016  | ·0020     | ·0000 | ·0010       | 1·25          | 2·39          | 1·78          | 1·85         | 0·63         | 0·55          | 0·29  |
| Mean ...        | —      | ·0005     | ·0004 | ·0009       | 0·22          | 0·33          | 0·39          | 0·86         | 0·91         | 1·18          |       |

\* *Loc. cit.*, vol. 99, p. 800.

of acid is generally *nil*, except when the formation of an acid salt is possible (sulphate); with organic salts, as much as from 0·17 to 2·4 equivalents of acid are absorbed, acidity appearing gradually. These values should really be about 50 per cent. higher, for the proper degree of acidity which should be selected as indicating the point at which absorption of acid ceases is that when further additions of acid cause no further increase in acid reaction; these values were recorded, as well as those applying to the first barely discernible change of tint, but they are more difficult of determination than those for the degree of acidity selected for the values in the Table.

The combination of acids with organic salts explains why the titration of an organic acid is generally impossible: but as the neutral complex formed is always partially hydrolysed, it will show some acid reaction, and the possibility of titration will depend on the delicacy of the indicator, as well as on the nature of the acid. Thus the following results were obtained:—

| Acid.          | Methyl orange.   | Litmus.         | Phenolphthalein.  |
|----------------|------------------|-----------------|-------------------|
| Tartaric ..... | 23 per cent. low | 4 per cent. low | Correct.          |
| Oxalic .....   | 32 " "           | 2 " "           | "                 |
| Acetic .....   | 80 " "           | 20 " "          | "                 |
| Lactic .....   | 20 " "           | 10 " "          | 10 per cent. low. |
| Citric .....   | Impossible       | 46 " "          | 33 " "            |

*Double Decomposition.*—An ato-compound with the same salt elements in both parts of the molecule—*e.g.*, a tartrato-tartrate—would be isomeric with the metallo and normal salts, and such ato-compounds figure in one of the four or five stages given below as occurring in double decomposition. They form jellies, or gelatinous precipitates, seen under the microscope to consist of membranous particles, illustrated in fig. 3, Plate 2, closely resembling, in miniature, the scale form of the hydrated metallo-compounds (fig. 1). They have been obtained in a dozen cases previously described.\* In many instances one or other of the following stages are passed too rapidly for recognition, and with inorganic salts it is generally only the last stage which is noticeable.

(1) The first stage when, for instance, barium chloride is gradually added to concentrated solutions of tartrate or citrate, consists of the precipitation of bari-tartrate as an emulsion: this rapidly redissolves. In other cases, previously investigated, the emulsion was sufficiently permanent to admit of its being analysed.

(2) It dissolves because it forms a highly soluble ato-compound with the

\* *Loc. cit.*, vol. 109, p. 248.

excess of potassium tartrate present, and the limit up to which dissolution occurs and the precipitation next described (3) begins\* on increasing additions of the barium salt, shows that its formula must be  $\text{BaT}, 3\text{K}_2\text{T}$  (ratio found,  $\text{Ba} : 3.12 \text{K}_2\text{T}$ ); in the case of the citrate it is  $\text{Ba}_3\text{Cit}_2, 3\text{K}_3\text{Cit}$  (ratios found,  $\text{Ba}_3 : 2.95 \text{K}_3\text{Cit}$  and  $\text{Ba}_3 : 3.1 \text{K}_3\text{Cit}$ ). [Alcohol added to these liquids precipitates the barium metallo-compound as an emulsion or solution, containing but little potassium. With the citrates, the solutions, if left for from 15 minutes to two hours, gelatinise, the jelly consisting of minute particles resembling bacteria (Plate 2, fig. 5). This contains a smaller proportion of the alkali metal citrate than that in the citrato-citrate in solution; the ratios found were  $0.67\text{--}0.93 \text{K}_3\text{Cit}$  and  $0.73\text{--}1.33 \text{Na}_3\text{Cit}$  to each  $\text{Ba}_3\text{Cit}_2$ . In some cases the metallato-compounds change directly into the corresponding normal double salts, and ultimately into the normal single salt;† in such an event the next stage is suppressed.]

(3) Continuing the addition of barium chloride, a gelatinous precipitate begins to form, soon rendering the mixture semi-solid. This is a metallato-compound of membranous structure, which, on analysis,‡ is found to contain no potassium or chlorine, and must, therefore, be isomeric with the metallo and normal salts. In solubility it is intermediate between them; the tartrato-tartrate dissolves to the extent of 0.7 grm. barium in 100 c.c. at  $10^\circ$ , the citrato-citrate, 0.13 grm.; the values for the normal salts are 0.096 and 0.032, respectively, whilst those for the metallo-compounds are indefinitely large.

(4) After some hours the normal salt begins to crystallise from the liquid, the bulky metallato-compound simultaneously re-dissolving, and disappearing entirely in a day or two. If only a small layer of the metallato-compound is present, the normal salt appears as isolated crystals, each in the centre of a circular area free from ato-compound. Similar indirect changes have been followed under the microscope (*loc. cit.*).

*Neutralisation* is but a special case of double decomposition, and the addition of barium hydroxide to tartaric or citric acid yields a series of compounds precisely similar to those mentioned above. The soluble ato-compound, in the case of the tartrate, is  $\text{BaT}, \text{H}_2\text{T}$ , but, in the case of the citrate,  $\text{Ba}_3\text{Cit}_2, 4\text{H}_3\text{Cit}$ . Such compounds, including the strontium analogue of this particular tartrate, have been isolated in several instances

\* The precipitate being somewhat soluble, especially in the case of the tartrate, the point at which it appears varies (in a nearly rectilinear function) with the dilution. Series of determinations, with different amounts of water present, gave the point at which it would first appear if no water were present to dissolve it.

† *Loc. cit.*, vol. 107, p. 948.

‡ For the method see *loc. cit.*, vol. 107, p. 949.

by precipitation with alcohol;\* their acid reaction is but feeble, being due merely to hydrolysis, the compounds themselves being neutral. They, too, like the potassium compounds, sometimes change into the isomeric normal salts—acid salts in this case—which are sparingly soluble and crystalline, *e.g.*, the acid tartrates and racemates of the alkali metals, which cannot be regarded as intermediate between the highly soluble neutral salts and the acids.

*Basic Metallato-compounds.*—The substitution of a metallic oxide for  $\text{H}_2\text{O}$  in the hydrato-compound (3), p. 536, should produce a basic or alkaline body. When concentrated tartaric acid is gradually added to baryta solution, some permanent precipitate is formed, and neutrality is attained before an equivalent of acid is reached. On dilution, the precipitate dissolves, and alkalinity reappears. With one equivalent to two of hydroxide, the precipitate approximates to  $3\text{BaT}, \text{BaO}$ , but varies in basicity, and also in solubility (from 0.1 to 0.45 grm. Ba in 100 c.c.), with the proportions taken. No analogous reaction occurs with citric acid, but basic cobalti-malate and citrate, as well as some twenty alkaline cupri-tartrates, have been isolated,† and it has been shown that, in the case of seven metals, the initial action of an alkali on their organic salts results in forming a soluble metallo-compound with  $\text{M}'\text{OH}$  in the place of  $\text{H}_2\text{O}$ .‡

*Mixed Metallato-compounds.*—The addition of barium chloride to mixtures of potassium citrate and sulphate results in a series of changes similar to those occurring in the absence of sulphate (p. 538), except that, when the barium reaches certain proportions, an opalescence—to be reverted to immediately—occurs before the permanent membranous precipitate forms. This latter consists of a sulphato-citrate, but, though some eighty preparations of it under different conditions were examined, no definite results as to its composition (beyond the probable existence of  $\text{Ba}_3\text{Cit}_2, 3\text{BaSO}_4$ ) were obtained. The compounds possible are very numerous.§ They contain no admixed barium sulphate (though they do so in the case of the tartrate), and are gelatinous, even when the proportion of barium as sulphate to barium as citrate is 4:1; also, the proportions in the precipitates are very different from those in the solutions yielding them, and the curves representing the variation of composition with conditions show undoubted breaks. In the case of the tartrate, the precipitate contains some tartrate under conditions such that, in the absence of sulphate, no tartrate would be precipitated.

\* *Loc. cit.*, vol. 109, p. 246.

† *Loc. cit.*, vol. 107, p. 946; vol. 101, p. 1616.

‡ *Loc. cit.*, vol. 109, p. 237.

§ Cf. *loc. cit.*, vol. 99, p. 801.

Taking varying proportions of potassium citrate and sulphate, the point at which ordinary barium sulphate makes its appearance in the membranous precipitate was determined by microscopic examination, which we owe to Dr. Hutchinson, to be  $2K_3Cit : 3 \pm 0.3K_2SO_4$ : up to this point, therefore, there can be no free sulphate present, and it must exist as a sulphato-citrate of potassium. The formation of such compounds explains why the presence of an organic salt interferes with the quantitative precipitation of barium sulphate, etc. No definite results were obtained by adding baryta to mixtures of sulphuric acid with tartaric or citric acids.

*Inorganic Metallo-compounds.*—The opalescence mentioned above consists of a membranous solid like the other ato-compounds (fig. 3, Plate 2), but contains the elements of barium sulphate only, being, therefore, a sulphato-barisulphate. On filtering through a very fine porous candle, it forms a translucent jelly, which may be washed by leaving it in a dialyser for many weeks. It becomes more opaque, but retains its gelatinous, adhesive character, without changing into the normal sulphate (which is shown in fig. 4).

That inorganic salts may exist in the condition of metallo-compounds has already been suggested in reference to the modifications of the double sulphate  $CuK_2(SO_4)_2^*$  and of ferric chloride.† It appears, also, that in certain cases (the iodates of potassium and sodium) alcohol precipitates the salt as an emulsion from its solution.

*Heat of Neutralisation.*—Thomsen's results, the seeming irregularities in which lead to important conclusions, are collected in Table III. The high values for sulphuric, selenic and hydrofluoric acids are omitted; the first two are erroneous, owing to the concentration having been too great,‡ though they cannot be corrected with sufficient accuracy for use here; there is probably a similar source of error as regards hydrofluoric acid, and also in a minor degree as regards those somewhat exceptionally high values which appear in the Table. The seven inorganic monobasic acids showing lowest values give a mean of 13,743 cal., which is practically identical with the mean (E) for the polybasic acids; the relative values in other cases, compared with this as unity, are entered in brackets.

\* *Loc. cit.*, vol. 99, p. 811.

† *Loc. cit.*, vol. 105, p. 480.

‡ *Loc. cit.*, vol. 55, p. 325.

Table III.—Heat of Neutralisation of Acids.

| Acid.                                               | 1st NaOH.         | 2nd NaOH.         | 3rd NaOH.         | 2 NaOH.   | Excess alkali. | Alkali absorbed by salt. |
|-----------------------------------------------------|-------------------|-------------------|-------------------|-----------|----------------|--------------------------|
| I.                                                  | II.               | III.              | IV.               | V.        | VI.            | VII.                     |
| HCl .....                                           | 13,740            | 13,743<br>(1·00)  |                   |           | 10 (2)         | 0                        |
| HBr .....                                           | 13,750            |                   |                   |           | —              | 0                        |
| HI .....                                            | 13,680            |                   |                   |           | —              | 0                        |
| HClO <sub>3</sub> .....                             | 13,760            |                   |                   |           | —              | 0·00012                  |
| HBrO <sub>3</sub> .....                             | 13,780            |                   |                   |           | —              | 0·00010                  |
| HIO <sub>3</sub> .....                              | 13,810            |                   |                   |           | 608 (1)        | 0                        |
| HNO <sub>3</sub> .....                              | 13,680            |                   |                   |           | 0 (1)          | 0·00026                  |
| HPO <sub>3</sub> .....                              | 14,380            |                   |                   |           | 2,124 (2)      | —                        |
| HClO <sub>4</sub> .....                             | 14,080            |                   |                   |           | —              | 0·00010                  |
| HPO <sub>2</sub> H <sub>2</sub> .....               | 15,160            |                   |                   |           | 115 (1)        | 0·00021                  |
| Mean A .....                                        | 13,982<br>(1·017) |                   |                   |           |                |                          |
| Formic .....                                        | 13,450            | 13,448<br>(0·979) |                   |           | —              | 0·00008                  |
| Acetic .....                                        | 13,400            |                   |                   |           | 15             | 0·00007                  |
| Propionic .....                                     | 13,480            |                   |                   |           | —              | 0·00020                  |
| Ethyl sulphonic .....                               | 13,460            |                   |                   |           | —              | —                        |
| Chloroacetic .....                                  | 14,280            |                   |                   |           | —              | 0·0011                   |
| Dichloroacetic ...                                  | 14,830            |                   |                   |           | —              | 0·0046                   |
| Trichloroacetic ...                                 | 13,920            |                   |                   |           | —              | 0·0030                   |
| Mean B .....                                        | 13,831<br>(1·006) |                   |                   |           |                |                          |
| Oxalic .....                                        | 13,844            | 14,434            |                   |           | 222 (2)        | 0·00016                  |
| Succinic .....                                      | 12,400            | 11,756            |                   |           | 228 (2)        | 0·00201                  |
| Malic .....                                         | 13,035            | 13,133            |                   |           | 584 (2)        | 0·00127                  |
| Tartaric .....                                      | 12,442            | 12,872            |                   |           | 531 (1)        | 0·00048                  |
| Aconitic .....                                      | 12,848            | 12,933            | 13,333            |           | 986 (3)        | —                        |
| Citric .....                                        | 12,672            | 12,773            | 13,537            |           | 3,743 (3)      | 0·00028                  |
| Mean C .....                                        | 12,874<br>(0·937) | 12,984<br>(0·944) | 13,435<br>(0·978) |           |                |                          |
| H <sub>2</sub> SO <sub>3</sub> .....                | 15,870            | 13,098            |                   | 2. 14,484 | 360 (2)        | 0·00006*                 |
| H <sub>2</sub> Se <sub>2</sub> O <sub>3</sub> ..... | 14,772            | 12,252            |                   | 2. 13,512 | 460 (2)        |                          |
| H <sub>2</sub> PHO <sub>3</sub> .....               | 14,830            | 12,618            |                   | 2. 13,724 | 402 (2)        |                          |
| H <sub>2</sub> PHO <sub>4</sub> .....               | 14,829            | 12,249            | 6,951             | 2. 13,589 | 1,251 (3)      |                          |
| H <sub>2</sub> AsHO <sub>4</sub> .....              | 14,994            | 12,586            | 8,336             | 2. 13,790 | 1,484 (3)      |                          |
| Mean D .....                                        | 15,059<br>(1·096) | 12,559<br>(0·914) | 7,644<br>(0·557)  |           |                |                          |

\* The sulphite is said to be strongly alkaline : when pure it is not so.

Table III—continued.

| Acid.                                                 | 1st NaOH.                            | 2nd NaOH.                              | 3rd NaOH. | 2 NaOH.              | Excess alkali. | Alkali absorbed by salt. |
|-------------------------------------------------------|--------------------------------------|----------------------------------------|-----------|----------------------|----------------|--------------------------|
| I.                                                    | II.                                  | III.                                   | IV.       | V.                   | VI.            | VII.                     |
| H <sub>2</sub> IH <sub>3</sub> O <sub>6</sub> * ..... | (5,150)                              | (21,440)                               |           | 2. 13,295            | 5,450 (3)      |                          |
| H <sub>2</sub> S <sub>2</sub> O <sub>6</sub> .....    |                                      |                                        |           | 2. 13,770            | —              |                          |
| H <sub>2</sub> SiF <sub>6</sub> .....                 |                                      |                                        |           | 2. 13,310            | 45,992 (10)    |                          |
| H <sub>2</sub> PtCl <sub>6</sub> .....                |                                      |                                        |           | 2. 13,610            | 120 (4)        |                          |
| Mean E .....                                          |                                      |                                        |           | 2. 13,756<br>(1·001) |                |                          |
| H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> † .....  | 1st and 2nd.<br>2. 14,322<br>(1·042) | 3rd and 4th.<br>2. 12,047 *<br>(0·876) |           | 4. 13,185<br>(0·960) |                |                          |
| Abnormally Low Values.                                |                                      |                                        |           |                      |                |                          |
| HSH .....                                             | 7,738                                |                                        |           |                      | 64 (1)         |                          |
| HClO .....                                            | 9,980                                |                                        |           |                      | —              |                          |
| HCN .....                                             | 2,770                                |                                        |           |                      | —              |                          |
| H <sub>2</sub> CrO <sub>4</sub> .....                 | 13,134                               | 11,586                                 |           |                      | 444 (2)        |                          |
| H <sub>2</sub> As <sub>2</sub> O <sub>4</sub> .....   | 7,300                                | 6,480                                  |           |                      | 1,800 (2)      |                          |
| H <sub>2</sub> CO <sub>3</sub> .....                  | 11,016                               | 9,168                                  |           |                      | 408 (2)        |                          |
| H <sub>2</sub> B <sub>2</sub> O <sub>4</sub> .....    | 11,101                               | 8,909                                  |           |                      | 630 (4)        |                          |
| H <sub>2</sub> SiO <sub>3</sub> .....                 | 4,316                                | 914                                    |           |                      | 182 (2)        |                          |
| H <sub>2</sub> SnO <sub>3</sub> .....                 |                                      | 9,670                                  |           |                      | 5,450          |                          |

\* The anomalous behaviour is explained by Thomsen by the existence of two acids, H<sub>4</sub>I<sub>2</sub>H<sub>6</sub>O<sub>12</sub> and H<sub>2</sub>IH<sub>3</sub>O<sub>6</sub>.

† The values for the 3rd and 4th NaOH were not determined separately.

*Alkalinity of Salts of the Alkali and Alkaline Earth Metals.*—If the organic salts of these metals exist partially in solution as metallo-compounds, the latter would unite with molecules of the normal salts, producing metallato-compounds (tartrato-tartrates, etc.), containing non-acidic hydroxyl with H displaced by K, etc., which, as in every other known case, would result in alkalinity. The alkalinity of organic salts is well known, and, as will be shown, cannot be explained by hydrolysis; but it is not so well known that a similar, though much feebler, alkalinity characterises all the so-called neutral inorganic salts of these metals. Table IV contains the results obtained at 70°, using well boiled water with pure litmus as indicator; the alkalinity is also recognisable with methyl orange slightly tinted with acid, and in some cases with phenolphthalein. In the cases marked \* the salt was purified by repeated crystallisation, or precipitation by alcohol, in platinum.

Results with a few organic salts are added for comparison. With these, the alkalinity increases with rise of temperature; with the inorganic salts, in six cases examined, there was no appreciable, or a barely appreciable, alteration in tint on cooling to  $10^{\circ}$ .

Table IV.—Alkalinity in Equivalents  $\times 10^5$  of a Gramme-Equivalent (or in brackets, a Gramme-Molecule) of Salt when Dissolved in 10 litres of Water.

| Salt.              | K.             | Na.            | Li.          | Ca.         | Sr.         | Ba.          | Mg.          |
|--------------------|----------------|----------------|--------------|-------------|-------------|--------------|--------------|
| Chloride .....     | 44*            | 58*            | 31*          | 72<br>(74)  | 115<br>(87) | 88<br>(74)   | 136<br>(118) |
| Bromide .....      | 42             | 57             | 58*          | —           | —           | —            | —            |
| Iodide .....       | 29*            | 46*            | —            | —           | —           | —            | —            |
| Chlorate .....     | 29             | 50             | —            | —           | —           | —            | —            |
| Bromate .....      | 48*            | 64*            | —            | —           | —           | —            | —            |
| Iodate .....       | 45*            | 60*            | —            | —           | —           | —            | —            |
| Nitrate .....      | 33             | 53             | 40*          | 85<br>(107) | 88<br>(88)  | 112<br>(116) | 145<br>(169) |
| Perchlorate .....  | 48             | 59             | —            | —           | —           | —            | —            |
| Sulphate .....     | 64*<br>(55*)   | 70*<br>(66*)   | 48*<br>(50*) | —           | —           | —            | 69<br>(81)   |
| Sulphite .....     | 29*            | —              | —            | —           | —           | —            | —            |
| Thiosulphate ..... | 64*            | 87<br>(98)     | —            | —           | —           | —            | —            |
| Oxalate .....      | 108<br>(288)   | —              | —            | —           | —           | —            | —            |
| Tartrate .....     | 141<br>(278)   | 149<br>(197)   | —            | —           | —           | —            | —            |
| Citrate .....      | 3100<br>(9940) | 2706<br>(9356) | —<br>(3806)  | —           | —           | —            | —            |
| Acetate .....      | 8140           | —              | —            | —           | —           | —            | —            |

The alkalinity of inorganic salts is roughly proportional to the dilution, that of a gramme-molecule and gramme-equivalent, each in 10 litres, being approximately the same; and this rough proportionality may extend over a considerable range of dilution, as the following values (p. 545) with sodium sulphate and potassium chloride show; but the increase in alkalinity slackens with extreme dilution, and also, in the case of sodium sulphate, disappears altogether with extreme concentration.

With organic salts, the alkalinity for the two concentrations given in Table IV is generally constant, but at high concentrations it decreases considerably, as with sodium sulphate.

That this alkalinity is due to loss of acid in the preparation of the salt is disproved by the results with sodium sulphate, also by the fact that potassium chloride gave constant values,  $42\text{--}46 \times 10^{-5}$ , when (*a*) washed with water, and dried without heating, (*b*) twice precipitated by alcohol, and similarly dried, (*c*) treated in this way twice again, (*d*) acidified, and twice

precipitated, (e) twice dissolved, evaporated, and heated for eight hours at 100°.

| Volume<br>containing<br>one<br>equivalent. | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub> . |                                           | KCl.        |                                           | KI.         |                                           |
|--------------------------------------------|-------------------------------------------------|-------------------------------------------|-------------|-------------------------------------------|-------------|-------------------------------------------|
|                                            | Alkalinity.                                     | $\frac{\text{Alkalinity}}{\text{Volume}}$ | Alkalinity. | $\frac{\text{Alkalinity}}{\text{Volume}}$ | Alkalinity. | $\frac{\text{Alkalinity}}{\text{Volume}}$ |
| litres.                                    |                                                 |                                           |             |                                           |             |                                           |
| 0·09                                       | 0                                               | 0                                         | —           | —                                         | —           | —                                         |
| 0·18                                       | 1                                               | 5·5                                       | 1·1         | 6·1                                       | 11·5        | 64                                        |
| 0·36                                       | 4                                               | 11·0                                      | 2·2         | 5·9                                       | 13·7        | 36                                        |
| 0·72                                       | 6                                               | 8·3                                       | 3·6         | 5·0                                       | 16·9        | 23                                        |
| 1·26                                       | 11                                              | 8·0                                       | 4·8         | 5·8                                       | 19·9        | 16                                        |
| 2·56                                       | 18                                              | 7·0                                       | 17          | 6·6                                       | 28          | 11                                        |
| 12·6                                       | 78                                              | 6·2                                       | 45          | 3·6                                       | 56          | 4·4                                       |
| 32·5                                       | 130                                             | 4·0                                       | 85          | 2·7                                       | 116         | 3·6                                       |
| 82·5                                       | 270                                             | 3·3                                       | 236         | 2·8                                       | 170         | 2·1                                       |
| 132·5                                      | 350                                             | 2·6                                       | 275         | 2·0                                       | 180         | 1·3                                       |

That some salts may be hydrolysed in solution is not questioned, but if this is to account for their alkalinity, some evidence of it should exist in the heat of neutralisation values, for hydrolysis is reversed neutralisation, and it should be much more marked with the strongly alkaline organic, than with inorganic salts. The heat of neutralisation, it is true, is somewhat less in the former than in the latter case, but this is explicable on other grounds (p. 547), and the deficit bears no relation to the alkalinity of the salt: thus:—

|                                         | Acetate.  | Citrate.  | Tartrate.  | Oxalate.   |
|-----------------------------------------|-----------|-----------|------------|------------|
| Deficit of heat of neutralisation ..... | —343 cal. | —749 cal. | —1086 cal. | + 396 cal. |
| Alkalinity of salt .....                | 0·08140   | 0·03100   | 0·00141    | 0·00108    |

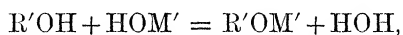
Moreover, if hydrolysis occurs, it will increase, and the heat of neutralisation decrease, as the proportion of base to acid is altered up to the point of equivalence. This is the case with the admittedly weak acids entered at the bottom of Table III (see also the rapidly diminishing values obtained by Thomsen on adding successive fractions of 1NaOH to silicic and boric acids); but no such decrease, indeed, a slight increase, is observed with the majority of organic acids (mean C, Table III), though their salts are strongly alkaline.

Whether hydrolysis occurs or not, it cannot account for alkalinity, unless the alkali affects the indicator more powerfully than does the acid. According to the conductivity and other properties, it should not do so in certain cases where alkalinity is conspicuous, for even in comparatively strong

solutions, hydrochloric and nitric acids, potash and soda, are all equally, and nearly entirely, ionised.\*

That acids and alkalis affect indicators equally, was proved by determining the minimum quantities recognisable by means of litmus, the observer being kept in ignorance as to which of the two tubes had had the reagent added to it. The acids examined were sulphuric, hydrochloric, nitric, oxalic, tartaric, citric, acetic and malic; the bases, potash, soda, lithia, lime, baryta and ammonia. In one series they all gave the limit as 1 to  $2 \times 10^{-6}$  equivalent per 100 c.c., in another 1 to  $2 \times 10^{-5}$  (dilutions of 1 equivalent in 700,000 and 70,000 litres, respectively): the reaction with the litmus being quantitative, the delicacy is increased by reducing the intensity of the coloration. With the faintest possible coloration, sulphuric, hydrochloric, citric and acetic acids all gave the limit as 2 to  $4 \times 10^{-7}$  (dilution, 3,500,000 litres), and with the strongest workable coloration,  $6 \times 10^{-5}$  (dilution, 17,000 litres), except acetic acid, which gave  $8 \times 10^{-5}$ . Slightly reddened methyl orange gave for these, and for oxalic and tartaric acids, and for potash and ammonia, 1 to  $2 \times 10^{-5}$ , acetic acid giving 2 to  $4 \times 10^{-5}$ . These dilutions embrace those of the alkali present in inorganic salts, which is about 20,000 litres in the values in Table IV, up to 180,000 litres in those given on p. 545.

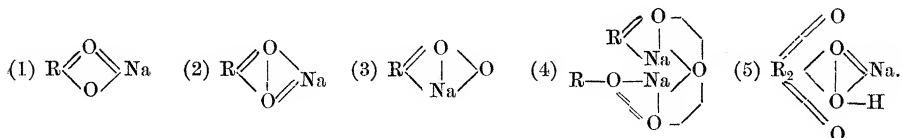
*Acids, Bases, and Salts.*—Acidity is conditional in organic acids, where our knowledge of constitution is soundest, on the presence of an hydroxyl side by side with a doubly bound oxygen atom. It is inconceivable that what is essential in this case should be immaterial in any other. It is equally inconceivable that this doubly bound oxygen atom, essential to acidity, should play no part in neutralisation. The neutralisation equation,



represents the action as being a double decomposition of the simplest character—an interchange between H and M' of union with one atom of oxygen for union with another—and should evolve no heat except that entailed in the conversion of a free molecule of water into part of a mass of liquid water, which is 8900 cal. at 18°. But the action cannot be a case of double decomposition, for it is not reversible, except in certain instances, and the heat evolved in it is 13,743 cal. Clearly, some affinity, not represented by this equation, becomes satisfied; this must be the residual affinity of the doubly bound oxygen atom, brought into play by the

\* Noyes, 'J. Amer. Chem. Soc.,' vol. 30, p. 345 (1908). The weakness of an acid or alkali in its action on an indicator is attributed, on the dissociation hypothesis, to its not being broken up into ions. A more obvious explanation is that it is not present as acid or alkali, but as anhydride, demonstrably so in such cases as  $CO_2$ ,  $H_2S$ ,  $H_3N$ ,  $HCN$ .

substitution of a metal possessing residual affinity, for hydrogen possessing none, the linkage in a normal salt being (1), or, more probably, (2),\*



It is known that the halide acids owe their acidity to the presence of water, and the present view will necessitate their containing the elements of  $2\text{H}_2\text{O}$ , *e.g.*,  $\text{H}_4\text{ClOOH}$ ;† an additional  $\text{H}_2\text{O}$  must also be assigned to a few other acids. The alkalinity of the salts is an important argument for the presence of two atoms of oxygen, for, being inexplicable on other grounds, it proves the presence of small quantities of ato-compounds. The halogens consequently must act as heptads, sulphur, etc., as octads in the sulphites (both already advocated by others on different grounds), and phosphorus, etc., as nonads in the phosphites; in all cases three stages beyond the lowest valencies.

The metallo-compound, with the higher valencies operating, will be depicted by the above formula (3), or, more probably, by the duplicated formula (4), which harmonises better with (2) (p. 536), and, as either of these represents a smaller number of valencies in operation than in the normal salt, it will agree with the fact (which the simpler formulæ on p. 536 did not) that the metallo-compound is the less stable of the two, as evidenced by its spontaneous transformation into the normal salt, and by the heat of neutralisation of organic acids, where the proportion of metallo-compound formed is large, being less than that of inorganic acids; the difference, taking the more uniform results (Table III, p. 542), is 2 per cent., or, taking all the results (means A and B), 1 per cent.

An acid salt might be intermediate between the acid itself and the neutral salt, but it certainly is not, for, whilst the full heat of neutralisation of a dibasic inorganic acid is strictly normal, there is a difference of 18 per cent. in the heat evolved by the two equivalents of base (Table III, mean D). On the dissociation hypothesis, neutralisation involves no

\* We must suppose that higher valencies do not come into operation when the same compound could exist without their doing so. If the normal salt were  $\text{R} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Na}$ , no rôle could be assigned to the doubly linked oxygen in neutralisation, and an acid salt would be exactly intermediate between the neutral salt and the acid, which it is not (*vide infra*).

† This does not negative the existence of some of the simple halide,  $\text{HCl}$ , in the solution. The remarkable colour changes of the copper and ferric halides (*loc. cit.*, vol. 105, p. 469) on dissolution and dilution show that they must exist in two fundamentally different conditions.

change but the deionisation of H and OH, and such a difference is impossible: but, on the present view, it can be explained, as shown in formula (5), by the residual valency of the other oxygen atoms, instead of that of the doubly bound oxygen, operating in the acid salt. But organic acids do not form acid salts in solution (p. 540), hence there is no such inequality in the successive addition of equivalents of base in their case (mean C); the first equivalent neutralises half the acid entirely, the metallo-compound uniting with the other half to form a metallato-compound; the second equivalent then neutralises the rest of the acid contained in this, and another metallato-compound, containing the elements of the normal salt, is formed. The reaction of both equivalents of base is the same, except for any small differences in the heat of formation of the two metallato-compounds from their proximate constituents, hence the successive evolutions of heat are nearly the same.

Without assigning an unacceptably high valency to phosphorus and arsenic, phosphoric and arsenic acids must be dibasic only, and they evidently are so, for a third equivalent of base evolves only half the normal heat, and the compounds formed are strongly alkaline. But pyrophosphoric acid might be tetrabasic, in spite of its containing only seven atoms of

oxygen, the linkage of three of the oxygen atoms being 
$$\begin{array}{c} \text{O} \\ | \\ \text{O} \begin{array}{l} \diagup \text{O} = \text{Na} \\ \diagdown \text{O} = \text{Na} \end{array} \\ | \end{array}$$

and the heat of neutralisation shows it to be so; it acts like a double molecule of a dibasic acid.

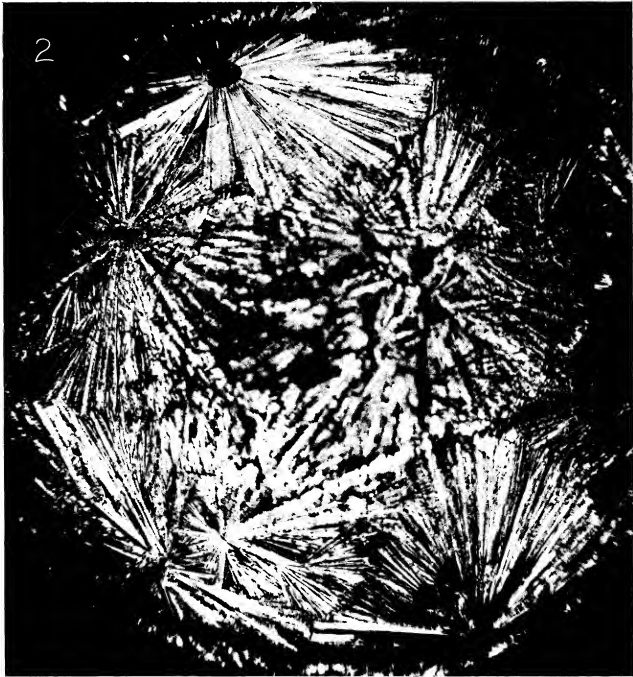
Since carbon exhibits no valency higher than 4, carbonic acid must be monobasic, and, certainly, bodies such as  $\text{Na}_2\text{CO}_3$  cannot be termed salts—the product of the neutralisation of an acid—for they are strongly alkaline, and alkalinity implies reversibility of the action by which Na has been substituted for H in the OH; hence this hydroxyl cannot have been an acidic hydroxyl.\* Addition of excess of alkali (excess being necessary with a reversible reaction) in such a case should evolve 8900 cal.; and, with one acidic and one non-acidic hydroxyl, as in carbonic acid, the evolution should be 22,643 cal.; this agrees approximately with the total of 20,592 evolved with a limited excess (Table III): boric acid gives 20,640 cal.† In all these

\* Subsequent investigation has showed that the molecular alkalinity of  $\text{K}_2\text{CO}_3$  and KOH is the same; hence both molecules must contain one “alkaline” potassium atom.

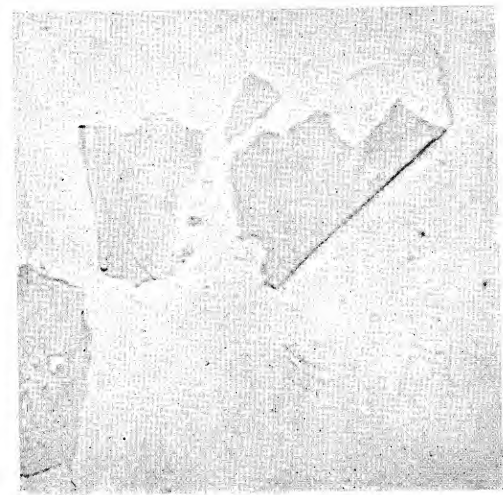
† The lowness of the value for the first equivalent of alkali proves the existence of some hydrolysis, even as regards the acidic hydroxyl. With chromic acid the values are nearly normal for both hydroxyls.



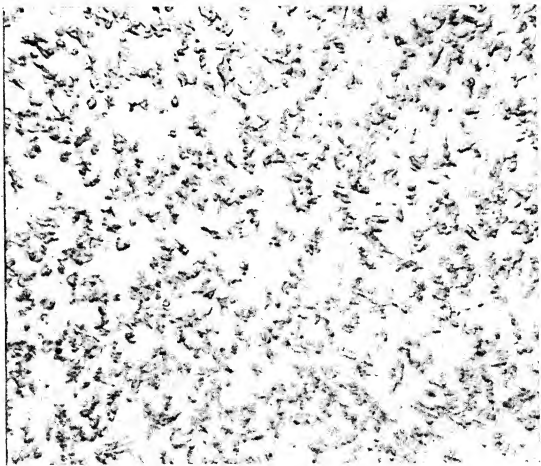
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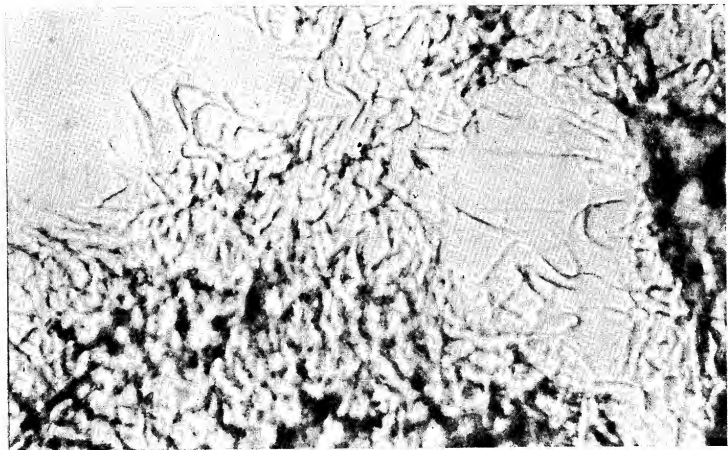
2



3.



4.



5.

cases of low values, the acids themselves are non-existent as definite compounds, and the so-called salts are strongly alkaline.

Little attention has ever been directed to the fact that alkalis combine with normal salts, evolving often a considerable amount of heat. Thomsen's values are given in Column VI (Table III), the numbers in brackets being the equivalents of alkali added; these have been supplemented (Col. VII) by determining the equivalents of alkali which must be added to the potassium salts before a definite alkalinity is produced, using the same method as that for investigating the combination of acids with salts (p. 537). This combination implies the conversion of  $R=O$  into  $R<\begin{smallmatrix} OH \\ OK \end{smallmatrix}$ , the compounds formed being analogues of basic salts.

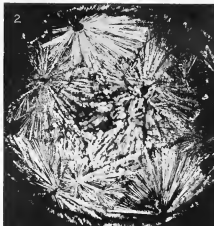
It is possible to estimate roughly whether the satisfaction of the residual affinities coming into operation according to the present views will account for the actual magnitude of the heat of neutralisation. To do so, it must be assumed, doubtless incorrectly, that the heat evolved on the satisfaction of each auxiliary valency is the same in every case, and that, with organic salts the product is entirely the metallato-compound, and with inorganic salts the normal salt. The differences between the heats of neutralisation of these two classes of acids, in the case of those which are mono- and poly-basic, gives 590 and 1756 cal., respectively (mean, 1,173 cal.), as the evolution on the satisfaction of one additional auxiliary valency [*cf.* formulæ (2) and (4), (p. 547)], so that in the formation of a normal salt, where three such valencies become saturated, (2), there would be an evolution of 3519 cal., which, with the heat evolved on the condensation of the water molecule, would give 12,419 cal., against the observed normal heat of neutralisation, 13,743 cal. A closer agreement could not be expected under the circumstances.

#### DESCRIPTION OF PLATE.

1. Soditartrate.   × 15 diam.
2. Sodium Tartrate.   × 15 diam.
3. Barium Sulphato-sulphate.   × 300 diam.
4. Barium Sulphate.   × 300 diam.
5. Potassium Citrato-baricitrate.   × 300 diam.



1.



2



3.



4.



5.

#### DESCRIPTION OF PLATE.

1. Soditartrate.  $\times 15$  diam.
2. Sodium Tartrate.  $\times 15$  diam.
3. Barium Sulphate-sulphate.  $\times 300$  diam.
4. Barium Sulphate.  $\times 300$  diam.
5. Potassium Citrate-barbitrate.  $\times 300$  diam.